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Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation

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ABSTRACT

One of the challenging issues faced by the modern world is the scarcity of fossil fuels, a result of the increasing use of fuel for transportation. Therefore, it is necessary to develop an alternative fuel source that can replace non-renewable fossil fuels. The use of biomass-derived fuels in place of conventional fuels is an emerging field of interest, and studies are on-going to find a solution to avoid a future energy crisis. Hydrodeoxygenation, which converts biofeed to hydrocarbon fuels that have all the qualities of conventional fossil fuels, is one of the most interesting and promising techniques in this field. The hydrodeoxygenation of vegetable oils to biofuel is an area in development. In the present paper, an overview of the catalysts used for hydrodeoxygenation of various vegetable oils is presented. In addition, the nature of the catalysts and reaction conditions necessary for the desired activity and selectivity of the catalysts are included. The current state of the field, trends in production processes and a brief description of commonly used feedstocks are presented as well.

Contents

1. Introduction

Oil scarcity, non-renewable resources, unpredictable prices and increasing environmental issues involved with petroleum-based fuels lead to the need for alternative sources to fulfill fuel needs [1]. Industry and transportation, especially air transportation, play crucial roles in increasing the emission of greenhouse gases, which cause global warming [2–4]. One fifth of the total oil produced is consumed by the transportation sector, including both land and air transportation [5]. A demand of 106.6 million barrels of biofuel is expected by 2030 [6].

The aviation industry has recently begun investigating alternative fuel sources to replace the conventional fuel, paraffin (also known as kerosene) from crude-oil reserves that are near depletion. Because this fuel is also shared with land transportation, the reserves will deplete quickly. The Kyoto Protocol in 1997 aimed to reduce greenhouse gases, such as CO_2, NO_X, CH_4, and SO_X, but current technologies and fuel requirements are not sufficient to

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uphold the protocol and result in increased greenhouse gas emissions [7,8]. To overcome the fuel crisis, the European Union (EU) proposed the 2003/30/EC and 2009/28/EC directives. The directives call for the substitution of conventional non-renewable transportation fuels with high-quality renewable biofuels [9].

Paraffin-based biofuel is getting major interest especially in aviation industries compare to diesel-base biofuel due to it satisfies the properties of conventional jet fuels. Paraffin-based biofuel are characterized by good cold flow properties, proper ratio of hydrocarbons (*n*-alkanes, isoalkanes, cyclo paraffins and aromatics) and high energy density [10]. It improved ignition and extinction characteristics, low aromatic content and sulphur content and perfect blending with conventional fuels [11]. When blended with conventional fuel, paraffin-based biofuel can be used in the same aircrafts or engine without further modifications. Besides, the usage would save environment by reduce air pollution and GHG emissions [12].

Biomass conversion into hydrocarbon fuel, or biofuel, has become an attractive solution to overcome this problem, as well as the environmental concerns of renewability, nitrogen and sulfur content and gas emissions in comparison to fossil fuels [13,14]. Currently, research is mainly concentrated on finding high-performance, eco-friendly, alternative second-generation biofuels that can replace conventional fuel without greenhouse gas emissions or causing a food crop crisis [15]. The main opposition to the use of cultivated crops for the production of biofuel is that it would affect the food chain. Farming of non-edible crops for fuel purposes can also adversely affect the food chain by utilizing water, land and fertilizer [16]. Despite these effects, this production process is relevant because it is an effective alternative to the use of fossil fuels.

Vegetable oils are a promising resource in the production of biofuel. Currently, focus is concentrated on non-edible vegetable oils. However, these vegetable oils cannot exactly replicate conventional fuels due to their high oxygen content (up to 50%), which leads to low heating value, immiscibility with fossil fuels, a tendency for polymerization, thermal instability and high viscosity [17,18]. The viscosity of vegetable oils can be lowered by chemical and thermal processes; however, the best-known process for lowering oil viscosity is pyrolysis, which leads to low-value products [19].

Catalytic hydroprocessing is a promising technology for the conversion of liquid biomass to biofuel. The process of catalytic hydrotreating involves the saturation of olefinic bonds and the removal of heteroatoms such as sulfur, nitrogen and oxygen [20]. Hydrodeoxygenation is the process of removing oxygen from oxygenated feedstocks, such as water [21]. Catalytic hydrodeoxygenation of vegetable oils results in hydrocarbon fuels with improved ignition qualities. Many research reports and patents focus on the conversion of fats and oils into biofuel. Jakkula et al. made use of fats in milk and vegetable oils, including rapeseed, sunflower, and canola oils, among others [22]. Petri and Marker used grease and vegetable oils [23], whereas Herskowitz claimed the use of both animal and vegetable oils as feedstock [24].

The present paper is an overview of the various metal catalysts used to produce paraffin-based biofuels by hydrodeoxygenation of vegetable oils. It is observed that the type of catalyst and nature of the feedstock influence the extent of hydrodeoxygenation and the efficiency of the fuel produced. The review also provides a glance into the current status and trends in vegetable oil hydrodeoxygenation, focusing on paraffin-based biofuels.

2. The feedstock

Typical feedstocks for second-generation biofuels are vegetable oils with high energy contents. The intention is to use vegetable oils directly as fuel [25]; however, the use of unmodified vegetable oils as the fuel is not efficient because of their high viscosity [26]. Although there are a number of vegetable oils available as feedstock, only soybean, palm, sunflower, safflower, cottonseed, rapeseed and peanut oils have been proven to have the potential to produce alternative fuels [27,28]. In developing countries, especially those in the Asian sub-continent, the production of edible vegetable oils is not sufficient, and so it is essential to use non-edible oil sources [29]. Rapeseed and sunflower oils are the main feedstocks used in Europe for biofuel generation. Palm and coconut oils are mainly used in the tropics, and soybean oil is used in United States [30]. The advantages of these oil seeds are their abundant oil content, better adaptation to growing conditions, regular maturation periods, low maintenance and formation of eco-friendly waste during oil extraction [28,30].

Camelina plants require little water and nitrogen for growth and can be cultured as a rotation crop for wheat. The plant needs less maintenance, such as the use of fertilizers [31]. The camelina seed contains approximately 40% oil, with the major content in

Table 1
Characteristics of the potential feedstocks used for biofuel production.

Feedstocks	Advantages	Disadvantages
Sunflower	More tolerant to low temperatures Can grow in a wide range of soil types [55] Can be cultivated as a rotational crop [56]	Edible oil Quality of oil depends on weather conditions and agricultural practices [57]
Rapeseed	Less used for food purposes Can grow on most soil types Can be cultivated over a wide range of temperatures [58]	Requires good drainage Easily attacked by diseases
Palm	Large scale production Long life span Less affected by climate Harvest throughout the year [59]	Edible oil Limited regional range due to high rainfall need Grow mostly in rain forest regions [60]
Soybean	Need optimum temperature Minimum water supply for growth [61] Large scale production [62]	Edible oil Requires extensive land and uses of pesticides [62]
Camelina	Need less water and fertilizer to grow Short growing season Can be grown as rotation crop for wheat By-product can be fed to animals [63]	Edible oil Depresses the growth of nearby plants [64]
Jatropha	Wide range of climatic suitability Large land volumes in subtropical regions Land use change can be carbon positive [60] Non-edible oil Long lifetime and less water consume [64] Draught resistant	No compatible production [64]

the oil being Omega-3 fatty acids [32–35], and 19 pounds of the seed produces one gallon of oil [36]. Camelina plant cultivation is primarily focused in Austria, Belgium, Denmark, Finland, France, Germany, Italy, Netherlands, Spain and UK [37].

Jatropha is a non-edible plant because of the presence of phorbol esters and can grow in infertile soil [38,39]. The jatropha plant is cultivated mostly in Central and South America [40,41], Africa and Asia [42]. Jatropha oil possesses a high kinematic viscosity, flash point, ignition point and solidifying point compared to conventional fuels.

Palm oil is widely used edible oil. Therefore, its utilization in fuel generation is not favored. Palm oil is mainly produced in Malaysia, and the Malaysian Palm Oil Board (MPOB) performed systematic studies on the production and evaluation of alternative fuel from palm oil and palm oil derivatives [43]. Malaysia plans to reduce its crude oil imports by promoting the use of palm oil for fuel production [44].

Sunflower seed oil is also edible oil in high demand, which has 40–50% oil content [36]. The largest producers of sunflower oil are the Ukraine, the EU-27, the Russian Federation, Argentina and Turkey [45]. Sunflowers only require a very short growing period compared to other oil crops, but the total worldwide production of sunflower oil is only 8% compared to the large production of soybean seed (55%), rapeseed (14%) and cotton seed (10%) [46].

Rapeseed oil, also known as canola oil, is the most widely use feedstock for biofuel generation. The main producers of rapeseed are China, Canada, India and Northern Europe [47]. They produce 7–10 million tons of canola seed per year. Canada exports 3–4 million tons of the seed and 800,000 t of canola oil per year [48].

The United States is the world's largest producer of soybean oil and is responsible for approximately 47% of the total global production [49]. Thirty-five million metric tons of soybean oil is produced worldwide [50]. The soybean plant is capable of nitrogen fixation by symbiosis; therefore, it requires less nitrogen fertilizers [51].

Waste cooking oil is the cheapest feedstock and can be accumulated from hotels, restaurants, bakeries, etc. Waste cooking oils have different properties compared to other virgin oils, especially in their free fatty acid content [52]. China produces the largest amount of waste cooking oil (500 million tons/year) from the catering industry [53]. The free fatty acid content in waste cooking oil is very high, which reduces its application for the generation of biodiesel [54], but the free fatty acid content does not affect the hydrodeoxygenation process.

Table 1 shows the merits and demerits of feedstocks that affect biofuel production.

3. Hydrodeoxygenation

First-generation biofuels, such as bioethanol from sugarcane and biodiesel palm oil, and second-generation biofuels such as bioethanol from waste biomass and biodiesel from waste cooking oil are not sufficient substitute for fossil fuels in large quantities to fulfill the required needs of all industries, especially the aviation industry. The main problems with these fuels were their low cetane numbers and lubricity, which lead to engine corrosion, instability in the presence of water and high hydrocarbon evaporative emission in addition to the food vs. fuel crisis that it arises. [65,66] Therefore, it is very necessary to develop new biofuels that fulfill engine needs. Hydrodeoxygenation is the process of increasing the energy value of the oil by the removal of oxygen as water [67]. During the hydrodeoxygenation process, unsaturated bonds in the fatty acid chains in the vegetable oils are saturated, and oxygen is removed in the form of water at an elevated temperature and pressure [68,69]. There are other alternative technologies for the upgrading of oil feedstocks, including catalytic cracking, emulsification, esterification, and steam reforming [70]. One competitive technology for the production of hydrocarbon fuel is the gasification of oil followed by Fisher–Tropsch (FT) synthesis. However, the major disadvantages of this process are the high cost and unfavorable carbon dioxide emissions [16]. The highly favored process is hydrodeoxygenation because of the formation of hydrocarbons in a narrow range of molecular weights [71]. Table 2 shows a comparison between the effectiveness of the gasification/FT process and hydrodeoxygenation methods. It is clear that the hydrodeoxygenation method gives better yields, even with a comparatively small amount of biofeed [72].

During the deoxygenation process, the bio oil feedstock can also undergo decarboxylation, i.e., the removal of oxygen from the feedstock in the form of carbon dioxide. The nature of the catalysts and reaction conditions can influence the route of this process. Hydrodeoxygenation is preferred under comparatively low temperatures and high hydrogen pressures [73]. Molecular sieve catalysts and supported metal catalysts in sulfided or reduced form are generally used for this purpose [74,75]. Supported noble metal catalysts generally favor the conversion of bio oil feedstocks into hydrocarbon fuels by decarboxylation, and sulfided or reduced catalysts favor the removal of oxygen via hydrodeoxygenation followed by the subsequent formation of the hydrocarbon fuel. The use of sulfided catalysts results in sulfur-contaminated fuel [76], and so the development of non-sulfided transition metal catalysts is necessary [77].

Hydrodeoxygenated products are characterized by a desired viscosity, low or no oxygen content, enhanced atomization and good lubricity [78,79]. The hydrodeoxygenation process increases the storage stability of oil-based energy sources [17]. The main goal of the hydrodeoxygenation process is to reduce the O/C ratio and simultaneously increase the H/C ratio [80]. During the process of hydrodeoxygenation, water is formed as the main by-product, which is favorable from an environmental pollution viewpoint but may affect the activity of the catalyst. Paraffin formed via the hydrodeoxygenation route exhibits improved properties compared to conventional fossil fuels. The high cetane numbers of *n*-alkane biofuels are promising for their use as commercial fuels [81]. Additionally, hydrotreatment can be executed in currently existing petroleum refineries with a low capital cost [81–84]. The hydrocarbon products formed show excellent low-temperature properties, such as cloud point and cold filter plugging point, when they contain a significant concentration of isomeric alkanes [85]. Occasionally, to improve the cold flow behavior or to modify the low-temperature properties of the

Table 2
Comparison between gasification/FT process and hydrodeoxygenation (HDO) method [72].

Plant type	Effective scale out put	Biomass input	Practical scale out put	Biomass input
HDO	> 400 ML	0.4 Mt/yr pongamia oil	150–400 ML	0.2–0.4 Mt/yr pongamia oil
G/FT	> 2000 ML	9.1 Mt/yr lignocellulose	400 ML	1.8 Mt/yr lignocellulose

hydrocarbon products, an extra isomerization step or the addition of flow modifiers is needed [9,86].

4. Mechanism of hydrodeoxygenation

The aim of the hydrodeoxygenation process is to upgrade oil by removing the oxygen content as water. The process includes treatment of oil at high pressures and moderate temperatures over heterogeneous catalysts. The use of vegetable oils, mainly non-edible vegetable oils, as feedstock for the hydrodeoxygenation process is highly favorable because their hydrocarbon content is in the same range as that of fossil fuels, such as kerosene and diesel. The fatty acids in vegetable oils are composed of straight chains of carbon atoms, and hydrodeoxygenation produces *n*-alkanes as the primary products [68,73]. The triglycerides in the vegetable oils are transformed into alkanes with water and propane as the by-products. Carbon dioxide or carbon monoxide is also obtained as a by-product when the reaction follows decarboxylation under hydrodeoxygenation conditions [87].

The rate of the hydrodeoxygenation reaction and its mechanism are influenced by the nature of feedstock used [15]. Oxygen removal includes C=O bond hydrogenation, C–O bond rupture and C–C bond cleavage, and larger hydrocarbons are selectively formed in the presence of a catalyst, which can cause C=O bond hydrogenation and C–O bond cleavage inhibiting C–C bond breaking [88].

The main factors that determine the selectivity of the reaction are the route of C–C and C–O bond cleavage and the extent of cleavage. The pathways for C–O bond cleavage were suggested to occur either through dehydrogenation to form surface-adsorbed species followed by direct cleavage catalyzed by metallic sites or via dehydration reactions catalyzed by acidic sites associated with the catalyst support [89,90]. Studies by Prasad and Bakshi explained the mechanism of the hydrodeoxygenation reaction and the formation of by-products [91]. The route of the reaction and products formed depend on the type of catalyst used [92]. The mechanism involves simple hydrodeoxygenation via an adsorbed enol intermediate, and the product is a straight-chain hydrocarbon with water and propane as the by-products.

The process of deoxygenation of triglycerides can be simply generalized as in Fig. 1. Deoxygenation can proceed through different routes, namely hydrodeoxygenation, decarboxylation/decarbonylation and hydrocracking. The hydrodeoxygenation reaction results in the formation of hydrocarbons with chains of the same number of carbons, along with water and propane. Hydrocarboxylation/hydrocarbonylation produces paraffin with one carbon less than that of the corresponding fatty acid and liberates CO_2 or CO. Hydrocracking forms shorter-chain alkanes [32,68,93–95].

The routes in Fig. 1 depend on the reaction temperature, pressure, liquid hourly space velocity and the catalyst used. The paraffins formed by hydrodeoxygenation pathway are isomerized. These products are characterized by a high cetane number and improved low-temperature properties. Decarboxylation products are *n*-alkanes with high cetane numbers, but they exhibit poor cold flow properties [96–100]. The hydrocarbon fuel produced from vegetable oils by the hydrodeoxygenation method is characterized by its improved properties compared to conventional petroleum-based fuels. The biofuel exhibits a high cetane number; however, the *n*-paraffinic fuel has poor cold flow properties. To improve the low-temperature properties, the *n*-paraffins are isomerized to isoparaffin. During the isomerization, the normal paraffin, with its high freezing point and outstanding cetane number, can be converted to isoparaffin, which has a far lower freezing point but retains a high cetane number [86,101]. Fig. 1 represents the possible deoxygenation pathways [81].

5. Catalysts used for hydrodeoxygenation of vegetable oils

The commonly used hydrodeoxygenation catalysts are supported noble and sulfided or reduced metal catalysts. Sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are widely used for hydrodeoxygenation, and it is reported that sulfidation generates active sites on the catalyst [102–104]. However, hydrodeoxygenation using

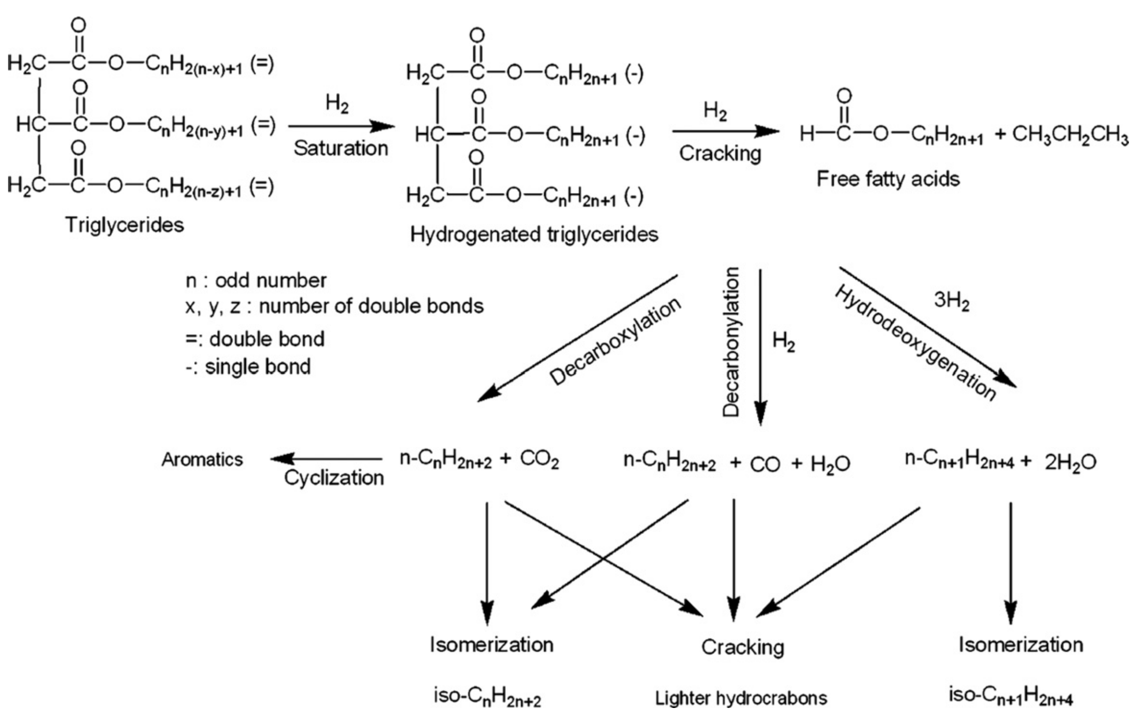


Fig. 1. The possible deoxygenation pathways [81].

sulfided catalysts is less favorable due to the formation of sulfur-contaminated products and the reduction of the catalysts in the low-sulfur reactant. In addition, noble metal catalysts are not favorable because of their high cost [105,106]. Therefore, more attention must be devoted to developing non-sulfided transition metal catalysts. Catalytic activity depends on the type of feedstock used, reaction conditions and nature of the catalysts. The acidic or basic sites on the catalyst support play the main role in activating the reactants and determining product selectivity [107]. The product selectivity and extent of hydrodeoxygenation also depend on the reaction temperature, pressure, H_2 to oil volume ratio and liquid hourly space velocity (LHSV). It is observed that the presence of water decreases the stability, activity and selectivity of the catalyst, which, in turn, decreases the degree of deoxygenation [108].

Sunflower oil has been used as an oil feedstock for hydrodeoxygenation over various catalysts. Krár et al. examined the catalytic hydrodeoxygenation of light gas oil containing 10% sunflower oil over an alumina-supported transition metal catalyst. The products formed were characterized by low sulfur and aromatic content. The paraffinic products showed good cold flow properties with a high cetane number. The studies were carried out under specific conditions (340–360 °C, 6–8 MPa, LHSV 1–3 h^{-1} and H_2 to feed ratio of 600 N m^3/m^3) [96]. They showed that sunflower oil could be effectively hydrotreated over reduced NiMo/γAl_2O_3 catalysts to obtain high paraffinic products at a high temperature range (360–380 °C) and pressure (6 MPa) and low space velocity of the oil feedstock. The resulting products consisted of C_{15}–C_{18}, which showed that the deoxygenation proceeded via both hydrodeoxygenation and decarboxylation, and also exhibited a high cetane number and poor low-temperature properties. At low temperatures and high pressures, hydrocracking dominated [109].

The same team presented the deoxygenation of sunflower oil over a reduced CoMo/Al_2O_3 catalyst at a temperature range from 300 to 380 °C, H_2 pressure of 4–6 MPa and space velocity of 1 h^{-1}. The catalyst was activated by reduction. At 380 °C, the conversion was 100% with 73.7–73.9% high paraffin yield. The high paraffin fraction consisted of *n*-alkanes and *i*-alkanes and possessed a high cetane number, higher than that of diesel fuel (103–104 at 300 °C), and excellent cold flow properties without any flow improvement additives. Therefore, the paraffinic products exhibited good blending properties (5–30%) with gas oil (Grade A) [9]. The authors tested the activity of non-presulfided CoMo/Al_2O_3 and NiMo/Al_2O_3 and observed that both of the catalysts exhibited high deoxygenation activity for the conversion of sunflower oil to paraffins. The observed yields of the target products were 72.7% and 49.6% for CoMo/Al_2O_3 and NiMo/Al_2O_3, respectively, at 380 °C, pH2 40 bars, LHSV 1.0 h^{-1} and H_2/sunflower oil volume ratio of 600 N m^3/m^3. Both the catalysts presented isomerization activity, and the isoparaffin contents of the total product were 25–44.5 wt% and 11.8–17.3 wt% for CoMo/Al_2O_3 and NiMo/Al_2O_3, respectively. Because of the high isoparaffin ratio, the fuels obtained had significant cold flow properties and high cetane numbers (89–91); therefore, they could be favorably blended with conventional petro fuel. The products were free from sulfur and nitrogen contamination and possessed less aromatic content. As a consequence of the high *i*/*n* paraffin ratio, the paraffin produced with CoMo/Al_2O_3 had comparatively advanced cold flow properties [86].

Duan et al. performed hydrodeoxygenation over 5 wt% Pd/Al-SBA-15 with varying Si/Al molar ratios (22–300) and Pd/HZSM-5(22). It was found that the activity of the catalyst depends on the catalyst acidity and reaction temperature. The highest activity was shown by Pd/Al-SBA-15 with Si/Al=300 74.4% liquid products at 250 °C, and the C_{15}–C_{18} hydrocarbon yield was approximately 72.9% at this temperature. At higher temperatures, the yield was not favored by increased catalytic acidity because of C–C bond cracking [110]. Harnos et al. focused on the use of non-sulfided catalysts and compared the activity with that of sulfided catalysts. The catalyst systems used in this study were Pd/activated C, Pd/Al_2O_3, Ni/Al_2O_3 and NiMo/Al_2O_3. The tests were carried out at 340 °C and 21 bars H_2 pressure. The obtained product distribution, i.e., the C17/C18 ratio, was affected by the route of the reaction. On supported Pd and Ni catalysts, decarboxylation dominated, and the main products were hydrocarbons with shortened-chain alkanes and low *i*-paraffin/*n*-paraffin ratios. Hydrodeoxygenation over NiMo/Al_2O_3 resulted in linear alkanes with comparatively higher *i*-alkane/*n*-alkane ratios (0.71 with 3% Ni). The non-sulfided catalysts exhibited higher activity compared with the sulfided catalysts [111].

Sankaranarayanan et al. hydroprocessed a mixture of sunflower oil and straight-run gas oil over sulfided NiO(3%)–MoO_3(12%)–γAl_2O_3 that incorporated 0.15 and 30 wt% zeolite beta at a temperature range of 320–350 °C under 3–6 MPa pressure. The catalyst with 30% zeolite beta achieved 100% conversion to hydrocarbons at 330 °C, 6 MPa and 2 h^{-1} space velocity compared to the NiMo/alumina catalyst without zeolite beta. Zeolite beta incorporation improved the hydrodesulfurization capacity of the catalyst. Maximum *n*-alkane (C_{18}) production was favored by the catalyst that incorporated 15% zeolite beta. Low temperature, high pressure and oil feed rate increased the C_{18} *n*-alkane formation. The catalysts showed good HDO performance towards free fatty acids [112].

Šimáček et al. carried out hydroprocessing of neat sunflower oil in a temperature range of 360–420 °C under 18 MPa pressure over conventional hydrocracking supported metal sulfide catalysts. The hydroprocessing resulted in hydrocarbons with low aromatic content. The concentration of *n*-alkanes (C_{17} and C_{18}) at 360 °C was 53 wt% and decreased to 5 wt% at 420 °C, and the concentration of *i*-alkanes and cycloalkanes increased to 73.5%. The composition of hydrocarbons formed at 420 °C was similar to petroleum-based diesel fuel and showed good cold flow properties (cloud point −11 °C and cold filter plugging point −14 °C). The products obtained at 400 and 420 °C were used for blending with conventional diesel fuel [85]. Hancsók et al. used reduced CoMo/Al_2O_3, NiMo/Al_2O_3 and NiW/Al_2O_3 for the production of bioparaffin from sunflower and rapeseed oil feedstocks. The highest yield was obtained with CoMo/Al_2O_3 (75–85%). The products showed high cetane numbers (>90) and good blending properties [113].

The goal of Tóth et al. was the production of hydrocarbon fuel with hydrocarbons in the diesel range by deoxygenation of a gas oil–sunflower oil mixture. It was established that products with less sulfur and less aromatic content were formed under the reaction conditions of 360–380 °C, 8 MPa, LHSV=0.75 h^{-1} and hydrogen/feedstock volume ratio=600 N m^3/m^3 with varying vegetable oil content (0–15%). The highest cetane number was obtained using 15% vegetable oil content. The isomerization of the products improved the low temperature properties of the products [114]. They extended the studies by performing co-hydrogenation of a mixture of gas oil (with high sulfur content ~1%) and sunflower oil (with different oil contents, 0–100%). The process was carried out over sulfided NiMo/Al_2O_3 at a temperature range of 300–380 °C and H_2 pressure 6–8 MPa. The catalyst increased vegetable oil conversion and gas oil upgrading. More than 95% yield was obtained with low aromatic and sulfur content under the following reaction conditions: T=360–380 °C, P=80 bars, LHSV=1.0/h and H_2/HC=600 N m^3/m^3 and up to 15% vegetable oil content of the feed. However, the low-temperature properties of the improved gas oil were poor, although they can be modified using additives. When the amount of vegetable oil

was >15%, desulfurization decreased. Due to increases in the *n* and *i* paraffin content, the product showed low emissions and good ignition properties [115].

Rapeseed oil is a widely used feedstock for the biofuel generation. Mikulec et al. investigated the activity of γAl_2O_3-supported NiMo and NiW sulfides for the conversion of refined rapeseed oil, refined sunflower oil, palm oil and crude tall oil into hydrocarbons. The catalysts typically used were hydrodesulfurization catalysts. By treating 6.5% vegetable oil and gas oil in a temperature and pressure range of 320–360 °C and 3.5–5.5 MPa, respectively, gas oil with 5–5.5% hydrocarbons (nC_{17}–nC_{18}) with same performance as petro diesel resulted. The rate of desulfurization of atmospheric gas oil was slower compared to *n*-alkane production over the present catalyst. The selectivity of the product increased with an increase in the reaction temperature [116].

Kubička et al. used sulfided Co and Mo supported on aluminum-incorporated mesoporous MCM-41 for the deoxygenation of refined rapeseed oil. Aluminum incorporation increased the conversion and selectivity, and the main products were *n*-heptadecane and *n*-octadecane, but the yield was lower compared to that over alumina support. This decrease in yield was mainly due to the difference in the interaction between the support and metal active phases in the two compositions. An increase in the hydrogen pressure led to hydrodeoxygenation over decarboxylation [15]. Kubička and Horáček performed the deoxygenation over the sulfided CoMo/-Al_2O_3 catalyst. The contents of the rapeseed oil feedstock, including alkalis and phospholipids, influenced the yield of reaction. The high concentration of the alkalis and phospholipids caused deactivation of the catalyst due to coking. Deoxygenation was carried out at 350 °C, 2 h^{-1} space velocity and 3.5 MPa hydrogen pressure and resulted in C_{18}–C_{17} hydrocarbons with varying C_{18}/C_{17} ratio. Sulfidation increased the selectivity of the reaction ratio by increasing catalytic acidity, which decreased the hydrodeoxygenation/decarboxylation ratio [71].

Kubička and Kaluža investigated the deoxygenation at 260–280 °C, 3.5 MPa and 0.25–4 h^{-1} space velocity with alumina-supported Ni, Mo, and NiMo sulfided catalysts. The highest activity was observed for the bimetallic NiMo/Al_2O_3 with a Ni/(Ni+Mo) ratio of 0.2–0.4% prepared by the impregnation method. The catalysts gave different product (*n*-octadecane and *n*-heptadecane) selectivity. NiMo/Al_2O_3 catalysts followed both the hydrodeoxygenation and decarboxylation routes with hydrodeoxygenation to decarboxylation product molar ratios of 1–3.5, which increased with an increase in conversion due to the formation of fatty acid ester intermediates. However, Ni/Al_2O_3 and Mo/Al_2O_3 selectively provided decarboxylated products and hydrodeoxygenated products, respectively [109]. Kubička et al. reported the application of organized mesoporous-alumina-supported CoMo catalysts (CoMo/OMA) for the hydrodeoxygenation process. The CoMo/OMA catalysts showed higher activity for deoxygenation compared to CoMo/MCM-41 and CoMo/Al_2O_3. The deoxygenation process followed a hydrodeoxygenation or decarboxylation route depending on the reaction temperature, pressure and nature of the support. The selectivity of the reaction was maximized at 310 °C under 7 MPa pressure. At high temperature and low pressure, decarboxylation was favored; C_{17} alkanes were the main product and C_{18}/C_{17} ratio decreased [117].

Šimáček et al. hydrodeoxygenated rapeseed oil over different Ni–Mo/alumina sulfided catalysts with varying Ni and Mo wt% at a range of temperatures from 260 to 340 °C under a hydrogen pressure of 7 MPa. The resulting liquid product contained C_{17} and C_{18} *n*- and *i*-alkanes. At low temperatures, the reaction was incomplete. Above 310 °C, the product selectively comprised hydrocarbons identical to those present in conventional diesel. There was an increasing trend in *i*-alkanes with an increase in temperature for all the catalysts, which was most clearly observed in the cases of the catalysts with NiO and MoO_3 of wt% 2.6 and 15.7, respectively [118]. Šimáček et al. hydrotreated the oil in the presence of the commercially available Ni–Mo/Al_2O_3 catalyst at the temperatures of 310 and 360 °C and hydrogen pressures of 7 and 15 MPa. The reaction products obtained at 360 °C under 7 MPa hydrogen pressure were approximately 75 wt% *n*-alkanes, *n*-heptadecane and *n*-octadecane. The products were characterized by high cetane numbers but exhibited poor cold flow properties while blended with mineral diesel even after the addition of flow modifiers [69].

Tth et al. reported the co-hydrogenation of a mixture of straight-run heavy gas oil and rapeseed oil in different combinations over NiMo/Al_2O_3 using the same reaction conditions. The highest conversion was obtained at 380 °C under 8 MPa of pressure, space velocity of 1.0 h^{-1} and hydrogen/oil feed ratio of 600 N m^3/m^3 with 0–20% rapeseed oil concentration. The product obtained was characterized by a high cetane number and good combustion properties, but the cold flow properties were very poor and the product required isomerization. Vegetable oil concentrations >20% reduced the desulfurization [119]. There are reports on the use of other oil feedstocks for in the hydrodeoxygenation process, such as palm oil, cooking oil, canola oil, soybean oil, etc. Guzman et al. hydrodeoxygenated palm oil using a sulfided NiMo/γAl_2O_3 catalyst, which is the conventional hydrodeoxygenation catalyst. The diesel-range hydrocarbon products were obtained at 4–9 MPa of hydrogen pressure. Low pressure resulted in the formation of intermediates [26]. Toba et al. studied the hydrodeoxygenation of waste cooking oil over sulfided catalysts. The activities of the catalysts were tested both in the liquid and gas phases. NiMo/Al_2O_3 CoMo/Al_2O_3 and NiW/Al_2O_3 catalysts were used for the study. Alumina-supported NiMo and NiW showed high activity for hydrodeoxygenation compared to CoMo/alumina because of deactivation of the latter. The suitable temperature for the hydrodeoxygenation was observed to be 350 °C. However, the NiW/Al_2O_3 catalyst resulted in mainly decarboxylation compared to the NiMo and CoMo catalysts. The sulfur content in the final hydrocarbon products was very low. The activity of NiMo/B_2O_3–Al_2O_3 was also tested, and it was observed that the acidity of the B_2O_3–Al_2O_3 support enhanced the formation of iso-paraffins (3.8% with NiMo/alumina and 7.5% with NiMo/B_2O_3–Al_2O_3), which is the main factor affecting the cold flow properties of hydrocarbon fuels [120].

Tiwari et al. used mesoporous SiO_2–Al_2O_3 and Al_2O_3 as supports for sulfided Ni–W/SiO_2–Al_2O_3 and Ni–Mo/Al_2O_3. With the aid of these catalysts, they performed the hydroprocessing of waste soya oil mixture with refinery oil. The Ni–W/SiO_2–Al_2O_3 catalyst favored hydrocracking and selectively produced paraffin-range hydrocarbons via decarboxylation and decarbonylation. The Ni–Mo/Al_2O_3 catalyst was selective for hydrotreatment and resulted in diesel-range hydrocarbons by following the hydrodeoxygenation pathway. The hydrocarbon fuels produced using the above-mentioned catalysts were characterized by high cetane numbers and suitable density. These improved characteristics are an advantage of the presence of mesoporous support [79].

Veriansyah et al. studied the influence of different catalysts on the hydroprocessing of soybean oil. The systems used for this study were sulfided NiMo/γAl_2O_3, Pd/γAl_2O_3, sulfided CoMo/γAl_2O_3, Ni/SiO_2–Al_2O_3, wt% Pt/γAl_2O_3 and Ru/Al_2O_3. The highest conversion of oil was obtained with sulfided NiMo/γAl_2O_3 (92.9%). The hydrocarbon fraction mainly comprised straight-chain *n*-C_{17} and *n*-C_{15} (>80%) as a result of Ni- and Pd-based catalysts. Hydrotreatment using CoMo catalysts showed improved isomerization and cracking, which resulted in isoalkanes. The NiMo and CoMo catalysts followed the hydrodeoxygenation pathway, and the Pd catalysts proceeded via decarboxylation. The NiMo and CoMo catalysts were found to be cost-effective [81].

Monnier et al. prepared nitrides of alumina-supported molybdenum, tungsten and vanadium and verified their activity for the hydrodeoxygenation of oleic acid and canola oil. Alumina-supported molybdenum nitride ($Mo_2N/\gamma Al_2O_3$) showed the highest activity for the conversion of oleic acid, with almost 100% conversion and ~100% oxygen removal at 380 °C under 7.15 MPa of hydrogen pressure. Normal alkanes were produced with a high cetane number and n-C_{17}/(n-C_{17}+n-C_{18}) molar ratio 0.24. When the reaction was continued for 450 h with canola oil at 400 °C and 8.3 MPa, approximately >90% oxygen removal was observed. It was concluded that the supported molybdenum nitride catalyst brought about oxygen removal by the hydrodeoxygenation route, while the vanadium catalysts followed the decarboxylation route [121].

Because fatty acids are the basic content of vegetable oils, the hydrodeoxygenation of fatty acids has also been studied. Madsen et al. investigated the hydrodeoxygenation of oleic acid and tripalmitin over 5 wt% $Pt/\gamma Al_2O_3$ at temperature ranges 250–325 °C in a molar ratio 1:3. The deoxygenation was followed not by hydrodeoxygenation but by decarboxylation. Comparing the activity of the catalysts $Pd/\gamma Al_2O_3$ and $Ni/\gamma Al_2O_3$, $Pd/\gamma Al_2O_3$ was found to be more active than $Ni/\gamma Al_2O_3$. The conversion of oleic acid showed dependence on temperature, and 100% conversion to C_{15}–C_{18} was obtained at 325 °C. Heptadecane (~80%) was selectively formed at 1 MPa H_2 pressure. Conversion of tripalmitin was restricted by the formation of palmitic acid as an intermediate. The difference in activity of the two reactants was mainly because of their different molecular sizes and diffusivities [122].

Deoxygenation of stearic, oleic and linoleic acids over mesoporous Pd/C was investigated by Simakova et al. at 300 °C. The deoxygenation process proceeded via decarboxylation, not by hydrodeoxygenation. The resulting hydrocarbons were in the conventional diesel range. The products resulting from stearic acid as the feedstock were C_{17} hydrocarbons, and in the cases of oleic and linoleic acids, C_{17} aromatics were preferred. This difference showed that the catalytic activity depends on the degree of unsaturation in the feedstock. Catalytic deactivation was evident in the results because of the formation of aromatic compounds. *N*-heptadecane was the major product from stearic acid; C_{18} fatty acid isomers and stearic acid were obtained from linoleic and oleic acids, respectively [123].

Deoxygenation of palmitic acid and stearic acid was performed by Lestari et al. using 4 wt% Pd/mesoporous C catalyst at 300 °C under H_2 pressure of 17 bars. The main products were C_{15} and C_{17} hydrocarbons for palmitic and stearic acids, respectively. The production process followed the decarboxylation route and was found to be independent of the carbon chain-length of the reactant feed [124]. The same team investigated the deoxygenation of tall oil over the same catalyst. Linear C_{17} hydrocarbons were obtained with a maximum selectivity of 95% [125]. The authors extended their work with SBA-15-supported Pd instead of C and investigated the activity of the prepared catalyst for the deoxygenation of stearic acid at the same temperature and pressure as used earlier. The highly ordered structure of SBA-15 and large surface area favored the conversion. The greatest activity was obtained for 3 wt% Pd/SBA-15, and n-heptadecane was obtained with 90% selectivity [87]. Table 3 shows examples of feedstocks used in the hydrodeoxygenation process, the type of reactor, the catalysts and reaction conditions.

6. Advantages of bioparaffin over fatty acid methyl esters and petrol fuels as aviation fuel

FAMEs, or fatty acid methyl esters, are mono-alkyl esters of long-chain fatty acids produced by the transesterification of fat or oil using ethanol or methanol [126]. Bioparaffin is produced by deoxygenation of the biomass feedstock. Alternative hydrocarbon fuels have several advantages over FAMEs as transportation fuel. FAMEs face the major disadvantages of poor heating value, low storage stability due to a high degree of unsaturation, corrosivity because of the presence of moisture, ease of hydrolysis, undesired low-temperature properties and relatively low energy content [115,127]. Oxygen content in biodiesel tends to provide additional oxygen leading to greenhouse gas formation [128]. Hydrocarbon fuels are mainly characterized by their cold flow properties. Hydrocarbon fuels from hydrodeoxygenation are recognized by high cetane numbers compared to FAMEs and conventional petroleum-based fuels [129].

Compared to FAMEs, hydrocarbon fuels exhibit excellent low-temperature properties and high heating value [112]. The low heating values of petroleum-based fuels are due to less exothermic ignition of oxygenated compounds [130,131]. The other main advantages of hydrocarbon fuels are the low capital and operating costs. The major by-product of the hydrodeoxygenation process is propane, which is desired over the glycerol formed as a by-product during biodiesel production [132,26]. Hydrocarbon fuels have better blending properties because they lack oxygen content and unsaturation. Hydrodeoxygenation is observed to be independent of the quality of the vegetable oil used, but the fatty acid content and extent of unsaturation largely affect the properties of biodiesel [6]. The high lubricity of the hydrocarbon fuel results from the complete removal of oxygen from the oil feedstock. Bioparaffin products have better oxidation stability and exhibit good blending properties with fossil fuels compared with FAMEs. It has been reported that the sulfur content and aromatic content in the hydrocarbon products are much less than in FAMEs [133–140].

7. Current status and trends

Although hydrocarbon fuel formed by hydroprocessing of biomass can contribute to the fuel needed for land transportation, industries are eagerly looking to use these fuels in the aviation transportation sector. Today, the hydroprocessing of lipids has become an evolving technology for the production of hydrocarbon-based biofuel. The process of hydrotreating (mainly hydrodeoxygenation) has led to many patents and patent applications. Brady et al. used canola oil, corn oil, soy oils, rapeseed oil, fish oil, sewage sludge etc. [141]. Marker et al. made use of catalyst systems that can tolerate water and can regenerate hydrogen [142]. Herskowitz et al. produced normal paraffins (C_{14}–C_{18}) with minor aromatic products from vegetable oils and animal fats [143]. Myllyoja et al. applied the hydrodeoxygenation method followed by isomerization to produce diesel-range hydrocarbons [144]. The same teams have many patents in this field [145–150].

The forecast of worldwide biofuel production by region from 2011 to 2021 shows that production will almost double by 2021 [151]. The world diesel and jet fuel requirements will increase to 5–6 million barrels of total consumption per day. UOP LLC72 and Eni S.P.A. produced drop-in-paraffin fuel by hydrotreating triglycerides and Honeywell marketed the fuel [152,153]. The Neste Oil NExBTL process mainly concentrates on pilot plant hydrotreatment of vegetable oils and waste fats for the generation of renewable fuel with reduced lifecycle production of carbon dioxide (40–80%) [154]. In addition, Singapore aims to produce 800,000 t of renewable diesel per year from palm oil [155]. Valero in America uses waste cooking oil and animal fats as the feedstock for fuel generation in collaboration with their partner Darling International [156]. Boeing and colleagues work on pilot-scale generation of hydrocarbon fuel for aviation from jatropha and camelina-like oil feedstocks [157]. Fig. 2 represents the annual

Table 3
Examples of feedstocks, reactor types, catalysts and reaction conditions.

Feedstock	Reactor type	Reaction temp (°C)	Hydrogen pressure (MPa)	Catalysts	Amount of oil	Refs.
Sunflower oil + gas oil	Bench-scale trickle-bed reactor	340–360	6–8	Sulfided Transition metals/Al_2O_3	1–3 h^{-1}	[96]
Sunflower oil	Tubular down-flow reactor	300–360	2–6	Commercial NiMo/γAl_2O_3	0.5–2 h^{-1}	[109]
Sunflower oil	Flow reactor plant	300–380	4–6	Reduced CoMo/Al_2O_3	1 h^{-1}	[9]
Sunflower oil	Flow reactor	300–380	2–8	Non-presulfided CoMo/Al_2O_3 and NiMo/Al_2O_3	1–3 h^{-1}	[86]
Sunflower oil	Autoclave	200	2	Pd/Al-SBA-15	0.5 g	[110]
Sunflower oil	Plug-flow reactor	340	2.1	Pd/activated C, Pd/Al_2O_3, Ni/Al_2O_3, NiMo/Al_2O_3	1–3 h^{-1}	[111]
Sunflower oil + straight-run gas oil	Fixed-bed reactor	320–350	3–6	Sulfided NiO(3%)–MoO_3(12%)–γAl_2O_3/zeolite beta	1–4 h^{-1}	[112]
Neat sunflower oil	Bench-scale fixed-bed reactor	360–420	18	Supported metal sulfides	49 g/h^{-1}	[85]
Sunflower + Gas oil	Tubular reactor	300–380	4–8	NiMo/Al_2O_3/P	0.75–3 h^{-1}	[114]
Sunflower + rapeseed oil	Fixed-bed flow-through reactor	360–380	6–8	Reduced CoMo/Al_2O_3, NiMo/Al_2O_3 and NiW/Al_2O_3	1–1.2 h^{-1}	[113]
Heavy gas oil + sunflower oil	Continuous-flow reactor	360–380	6–8	Sulfided NiMo/Al_2O_3	1 h^{-1}	[110]
Rapeseed oil + Sunflower oil + palm oil + tall oil	Continuous-flow reactor	320–360	3.5–5.5	Sulfided NiMo/γAl_2O_3 and NiW/γAl_2O_3	1 h^{-1}	[116]
Rapeseed oil	Fixed-bed reactor	300 320	2–11	Sulfided MoO_3/CoO/MCM-41	1–4 h^{-1}	[15]
Rapeseed oil	Fixed-bed tubular reactor	350	3.5	Sulfided CoMo/γAl_2O_3	2 h^{-1}	[71]
Rapeseed oil	Fixed-bed reactor	260–280	3.5	Sulfided Ni/alumina Mo/alumina and NiMo/alumina	0.25–4 h^{-1}	[95]
Rapeseed oil	Fixed-bed reactor	250–350	0.7–7	Sulfided CoMo/OMA	1.5 h^{-1}	[117]
Rapeseed oil	Flow reactor	260–340	7	Sulfided Ni–Mo/alumina	1 h^{-1}	[118]
Rapeseed oil	Bench scale flow reactor	310, 360	7, 15	Ni–Mo/alumina	1 h^{-1}	[69]
Rapeseed oil + gas oil	Continuous flow reactor	320–380	6–8	NiMo/Al_2O_3	1 h^{-1}	[119]
Palm oil	Trickled-bed reactor	350	1.5–9	Sulfided NiMo/γAl_2O_3	2 h^{-1}	[26]
Waste cooking oil	Fixed-bed flow reactor	350	5	Sulfided NiMo/Al_2O_3 CoMo/Al_2O_3, NiW/Al_2O_3, NiMo/B_2O_3–Al_2O_3	2.8 h^{-1}	[120]
Waste soya oil + gas oil	Fixed-bed reactor	340–380	5	Sulfided Ni–W/SiO_2–Al_2O_3 and Ni–Mo/Al_2O_3	2.4 h^{-1}	[79]
Soybean oil	High-pressure batch reactor	400	9.2	Sulfided NiMo/γAl_2O_3, Pd/γAl_2O_3, sulfided CoMo/γAl_2O_3, Ni/SiO_2–Al_2O_3, Pt/γAl_2O_3 and Ru/Al_2O_3	28.1 g	[81]
Oleic acid, canola oil	Continuous-flow micro reactor	380–410	7.15	Mo_2N/γAl_2O_3, VN/γAl_2O_3, WN/γAl_2O_3	0.45 h^{-1}	[121]
Stearic acid + palmitic acid	Autoclave	300	1.7	Reduced Pd/C	0.05 M	[124]
Stearic acid	Semi-batch reactor	300	1.7	Pd/SBA 15	0.05 M	[87]

biojetfuel yields from different feedstock. It shows that palm oil is the most productive with more than 200 GJ/ha productions per year followed by coconut and jatropha. This is probably due to palm oil is the most commercial vegetable oil and biggest production in the world for the time being.

8. Problems and future outlook

The major challenge associated with the conversion of vegetable oil feedstock to hydrocarbon fuels is the availability of the oil. Current worldwide vegetable oil production per annum is not sufficient to provide fuel for all transportation needs. Fig. 3 shows the total world production of vegetable oil is 143.15 million tons with the biggest portion from palm oil, 33.6%. Palm oil demand is growing continuously due to its potential as biofuel and has surpassed soybean oil because it contains trans-fatty acids [159].

The use of edible oils for fuel generation will cause a food crisis. Therefore, it is necessary to use alternative non-edible vegetable oils, such as jatropha oil, pongamia oil, castor oil, nagchampa oil, or rubber seed oil. However, the increase in the demand for non-edible food crops may lead to deforestation, which in turn will affect the food chain as a result of space requirements. Most non-edible crops have the advantage that they can grow in infertile soil with fewer provisions, such as fertilizer or water. Until now, researchers have been looking for the technology to increase oil yield and production from non-edible crops, which is far less than palm oil production. As shown in Fig. 3, the total production of vegetable oils worldwide is 143.15 million tons (2011/2012 productions) [159].

The other problem is the use of appropriate catalysts for the catalytic conversion of vegetable oils. Commonly used catalysts are supported metal sulfides. Sulfided catalysts are found to be highly active and selective for the conversion of feedstocks, but the products are contaminated with sulfur. Also, low sulfur-containing feedstock cannot be hydrotreated. Another group of active catalysts are supported noble metal catalysts. Although they are highly selective for the process, their cost is the main factor that prevents their use on the industrial scale. Therefore, the development of cost-effective non-sulfided supported metal catalysts is necessary. Another issue is side reactions, such as decarboxylation/decarbonylation, along with hydrodeoxygenation. Usually the products formed via decarboxylation possess as good cetane numbers as the

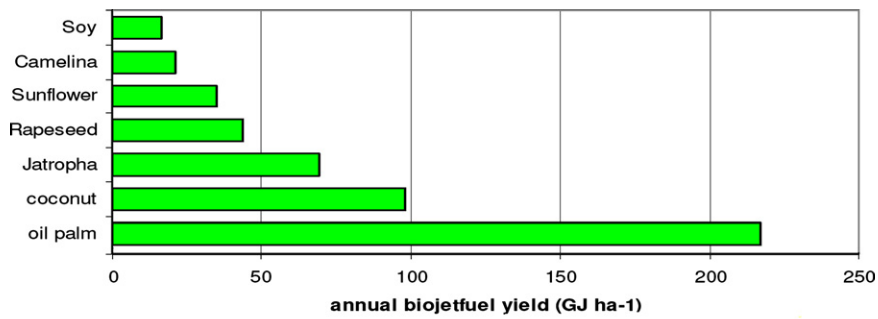


Fig. 2. Annual biojetfuel yields from different feedstock [64,158].

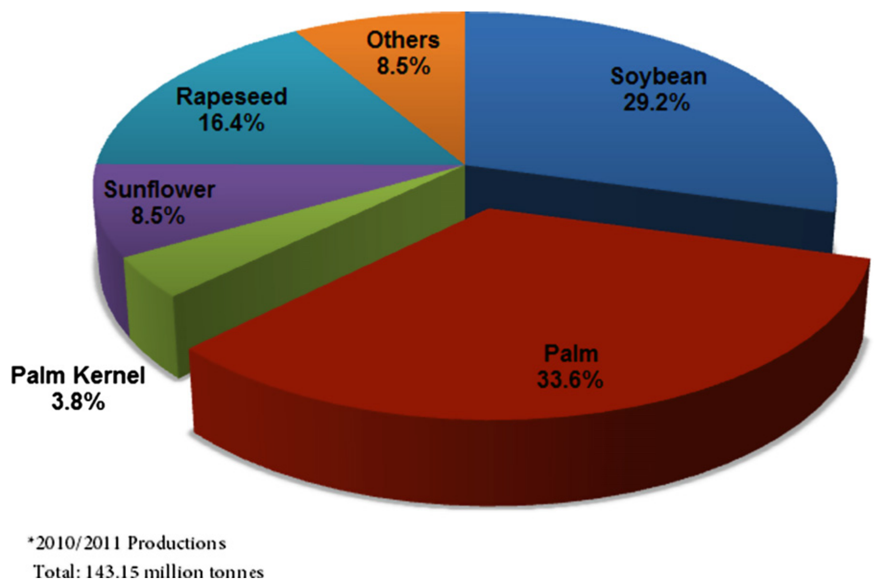


Fig. 3. World production of vegetable oils, total production 143.15 million tons (2011/2012 productions) [159].

hydrodeoxygenation products but show poor low-temperature properties, such as cloud point. The route of the reaction mainly depends on the reaction parameters and type of catalysts used. Therefore, highly efficient and selective catalysts should be discovered, which can decrease the process costs by decreasing the high temperature and H_2 pressure requirements.

9. Conclusion

The hydrodeoxygenation of vegetable oil is a promising route to the production of future fuels. The major advantage of the process is the formation of hydrocarbon products at the conventional fuel range. Generally, supported noble metal catalysts, sulfided metal catalysts and reduced metal catalysts are used for this purpose. All the categories of catalysts were found to be active for deoxygenation of the oil feedstock; however, the use of reduced metal catalysts on suitable supports has been shown to be the most convenient because the noble metal catalysts are not cost-effective, and sulfided catalysts result in sulfur-contaminated products. In addition to the deoxygenation of oil feedstock via a hydrodeoxygenation pathway, oxygen elimination can also occur by decarboxylation or decarbonylation. The main route of deoxygenation is determined by reaction parameters, such as the nature of the catalyst, reaction temperature, pressure, and amount/concentration of feedstock. Although the process requires elevated temperature and hydrogen pressure, it should be modified in such a way that the biofeed can replace non-renewable fossil fuels.

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